CURING, MECHANICAL AND AGING PROPERTIES OF BENTONITE FILLED ETHYLENE PROPYLENE DIENE MONOMER COMPOSITES

by

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TABLE OF CONTENTS

CHAPTER THREE: MATERIALS AND METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Standard for Testing and Materials
EPDM	Ethylene Propylene Diene Monomer Rubber
NR	Natural Rubber
BR	Butadiene Rubber
SBR	Styrene Butadiene Rubber
NBR	Nitrile Butadiene Rubber
ENR	Epoxidised Natural Rubber
MBT	2 mercapto benzothiazole
MBTS	Dibenzothiazole disulfide
MMT	Montmorillonite
oMMT	Organomontmorillonite
phr	Part per hundred rubber
Si69	Bis-(3-triethoxysilylpropyl) tetrasulfide
APTES	3-(aminopropyl)triethoxysilane
FESEM	Field Electron Scanning Microscope
FTFT	Fatigue-to failure test machine
rpm	Rotation per minutes
J.I.S	Japanese Industrial Standard Average
Bt	Bentonite
$CaCO_3$	Calcium Carbonate
Fe_2O_3	Iron Oxide
MgO	Magnesium Oxide
Al_2O_3	Aluminium Oxide

$Bt/CaCO_3$	Ratio of Bentonite to Calcium Carbonate
EPDM/NR	Ratio of Ethylene Propylene Diene Monomer to Natural Rubber
Ca^{2+}	Calcium ion
CaO	Calcium Oxide
K_2O	Potassium Oxide
Na^{2+}	Sodium ion
K^{+}	Potassium ion
-OH	Hydroxyl group
-SiOH	Silanol group
Al^{3+}	Aluminium ion
Fe^{2+}	Iron ion
Mg^{2+}	Magnesium ion

LIST OF SYMBOLS

Å	Amstrong
g/mol	Gram per molecule
%	Percentage
g cm^{-1}	Gram per centimeter
cm^{-1}	Per cm
g/m^2	Gram per meter square
^0C	Degree Celsius
mm	Millimeter
cm	Centimeter
g	Gram
µm	Micrometer
nm	Nanometer
t_{90}	Optimum cure time
ts_2	Scorch time
MH	Maximum torque
ML	Minimum torque
N/mm	Newton per millimeter
h	Hours
Hz	Hertz
dNm	Deci Newton meter
mm/min	Millimeter per minutes
N	Newton

SIFAT-SIFAT PEMATANGAN, MEKANIKAL DAN PENUAAN KOMPOSIT ETILENA PROPILENA DIENA MONOMER TERISI BENTONIT

ABSTRAK

Tujuan kajian ini adalah pertama, untuk menyiasat kesan pembebanan bentonit (Bt), kedua, pengantian separa Bt oleh kalsium karbonat ($CaCO_3$), ketiga, pengubahsuaian Bt oleh bis (3-trietoksisililpropil) tetrasulfida (Si69), dan akhir sekali, kesan campuran nisbah etilena propilena diena monomer (EPDM)/ getah asli (NR) atas sifat-sifat pematangan, sifat koyak dan penuaan serta hayat fatig komposit EPDM terisi Bt. Komposit EPDM terisi Bt disediakan dengan mesin penggiling bergulung dua dan dimatangkan pada 150^0C. Sifat-sifat pematangan komposit dikaji dengan menggunakan mesin Rheometer dan sifat-sifat mekanik ditentukan menggunakan Instron dan mesin ujian 'Fatigue-to-Failure'. Hasil kajian mendapati bahawa penambahan bentonit telah mengurangkan masa skorj (ts_2) dan meningkatkan masa pematangan (t_{90}), tork maksimum (MH), dan tork minimum (ML) komposit EPDM/Bt. Kekuatan koyak dan sifat penuaan (berdasar kepada peratusan pengekalan) masing-masing bertambah baik sehingga 90 bsg dan 70 bsg Bt, tetapi hayat fatig komposit EPDM/Bt berkurang. Penggantian separa Bt oleh $CaCO_3$ telah mengurangkan ML dan meningkatkan ts_2, t_{90}, dan MH. Kekuatan koyak dan hayat fatig menurun tetapi sifat penuaan menaik dengan meningkatnya $CaCO_3$ di dalam nisbah pembebanan Bt/$CaCO_3$ bagi komposit EPDM/Bt/$CaCO_3$. Hasil dari komposit EPDM/Bt yang telah diubahsuai dengan Si69, ts_2 meningkat sedikit manakala t_{90} berkurang. Kedua-dua MH dan ML didapati meningkat sehingga 0.5 bsg Si69. Sifat penuaan komposit EPDM/Bt meningkat dengan meningkatnya Si69. Kekuatan koyak dan hayat fatig komposit EPDM/Bt meningkat sehingga 0.5 bsg Si69. Peningkatan

NR di dalam nisbah adunan EPDM/NR telah mengurangkan ts_2, t_{90}, dan ML tetapi meningkatkan MH komposit EPDM/NR/Bt. Kekuatan koyak dan hayat fatig meningkat tetapi sifat penuaan berkurang dengan meningkatnya NR di dalam nisbah adunan EPDM/NR komposit EPDM/NR/Bt.

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ABSTRACT

The aims of this research were firstly, to investigate the effect of bentonite (Bt) loading, secondly, the partial replacement of Bt by calcium carbonate ($CaCO_3$), thirdly, the modification of Bt by bis (3-triethoxysilylpropyl) tetrasulfide (Si69) and the last one, the effect of blend ratio of ethylene propylene diene monomer (EPDM)/ natural rubber (NR) on the curing characteristics, tear and aging properties as well as fatigue life of bentonite filled EPDM composites. EPDM/Bt composites were prepared by two roll mills and vulcanized at 150^0C. The curing characteristics of the composites were investigated by using rheometer and mechanical properties were determined by using Instron and fatigue-to-failure test machine. It was found that addition of Bt decreased scorch time (ts_2) and increased optimum cure time (t_{90}), maximum torque (MH) and minimum torque (ML) of EPDM/Bt composites. Tear strength and aging property (based on retention percentage) improved up to 90 phr and 70 phr Bt, respectively but fatigue life of EPDM/Bt composites decreased. The partial replacement of Bt by $CaCO_3$ decreased ML and increased ts_2, t_{90}, and MH. The tear strength and fatigue life decreased but aging property increased with increasing of $CaCO_3$ in Bt/$CaCO_3$ ratio loading of EPDM/Bt/$CaCO_3$ composites. As EPDM/Bt composites were modified with bis (3-triethoxysilylpropyl) tetrasulfide (Si69), ts_2 was slightly increased meanwhile t_{90} decreased. Both MH and ML were found increased up to 0.5 phr Si69. The aging property of EPDM/Bt composites increased with increasing Si69. The tear strength and fatigue life of EPDM/Bt composites increased up to 0.5 phr Si69. Increasing NR in blend ratio of EPDM/NR

decreased ts_2, t_{90} and ML while increased MH of EPDM/NR/Bt composites. The tear strength and fatigue life increased but aging property decreased as NR increased in EPDM/NR blend ratio of EPDM/NR/Bt composites.

CHAPTER ONE
INTRODUCTION

1.1 Overview

The improvement in properties obtained by Toyota groups on polymer/clay nanocomposites has made the study based on clay nanocomposites been a focus of attention for the other scientists to further explore and this include the studies on rubber/clay based nanocomposites. The great improvement in this rubber/clay nanocomposites being studied have been ascribed to the possible reinforcement exhibited by the addition of organoclay in the nanocomposites itself. Clays in general consist of layered silicates. One of the examples of layered silicate is Bentonite. Bentonite comprised of montmorillonite in major parts of its constituents, and with the presence of small amount of quartz, biotite and feldspar (Ismail and Mathialagan, 2012). Bentonite is hydrophilic in nature. This is attributed to the presence of MMT that consists of silanol groups on its surface, with relatively weak forces in between their interlayer and therefore they are hydrated and highly polar. The addition of clay in rubber composites can have a great effect on the mechanical properties and characteristics of the composites. Enhanced properties of the nanocomposites usually are obtainable at low amount of filler. There are many studies reported in the past to have utilized bentonite as filler in the polymeric material. The difference level of polarity between rubber and inorganic materials can be a matter of problem in the composites as the difficulty may arise from the effort in order to obtain optimum interfacial interaction between the two. It is essential that the clay is treated or modified as to enable the clay to be compatible to the rubber matrix. Several attempts

have been studied to explore for a suitable compatibilizer in corresponding to overcome this problem (Alkadasi et al., 2005; Ge et al., 2015; Sabatini et al., 2015). Researchers also try to hybrid between two or more fillers (Qian et al., 2008; Sikong et al., 2015; Razzaghi-Kashani & Samadi, 2015) and blending with other elastomeric materials (Sahakaro et al., 2008; Pticek et al., 2007; Vijayalekshmi & Abdul Majeed, 2013). All these methods are the alternatives in order to find new and cheap materials that can improve and maintain the desirable end properties of rubber/clay composites.

In some applications where cost is important, Bt is considered fairly expensive and high loading of Bt are also required to achieve certain properties (Mathialagan & Ismail, 2011). Partial replacement of Bt by a much cheaper non-black filler such as calcium carbonate is therefore needed in order to reduce the cost as well as the weight of the rubber composites, which in this research, ethylene propylene diene monomer (EPDM) rubber is used. EPDM is one of the most important synthetic rubbers that are widely used in the advance of rubber industry. They found their vast applications in commodity and also specialty products in the market such as in automotive application, construction, and building profiles. For example, EPDM is used widely as tire sidewalls, window and door seals, hose and tubing, roof membranes, wire and cable insulators, gasket and even in footwear (Salamone, 1999). EPDM is a very nonpolar type of rubbers having a saturated polymer backbone. Their low level of unsaturation makes them having an excellent resistance to heat, aging and oxidation. EPDM also has a high thermal stability and electrical resistivity, besides having a low temperature flexibility and ability to accept high filler loading.

1.2 Problem Statements

In order to optimize the properties of the composites so that it satisfies the requirement of certain applications, the uses of filler that have a reinforcing effect to the rubber composites are necessary. Among the reinforcing filler used to improve the processing characteristics and mechanical properties of the vulcanizate, carbon black has been the most important filler among many types of fillers. However, the inability to alter the final colour of the products limits the use of carbon black in certain application. Besides, carbon black also is very dependent on the petroleum feedstock which therefore increased the cost of the materials. These limitations have then shifted the interest of the researchers to find non-black filler that can give a significant improvement to the rubber vulcanizate.

Examples of non black fillers are such as silica, calcium carbonate, and clay. Bentonite is in smectite clay group that is reinforcing but in order to have certain properties, they need to be used in high loading. As compared to other type of clays such as kaolin and illite clay, bentonite has high absorption of water, able to adsorb and absorb toxin and impurities and has high pH making it the most advantageous clay and therefore is consider being costly in commercial, hence there is a need to hybrid bentonite with fillers that is much cheaper. Incorporation of $CaCO_3$ to replace partially the use of Bt able to reduce the cost of EPDM composites. In another aspect, eventhough Bt able to enhance the properties of the composites, the researchers found that the use of Bt can result in a poor dispersion especially in non-polar rubber matrix such as EPDM. This is attributed to the problem of polarity different between polar clay and nonpolar rubber matrix that results them to be incompatible to each other. Considering this setback, therefore, there is a need to modify the surface of Bt

so that the interaction between Bt and EPDM matrix can be improved. One of the ways that can be used are by using silane coupling agents such as (3-aminopropyl)triethoxysilane (APTES) and Bis-(3-triethoxysilylpropyl)tetasulfide (Si69). Si69 are reported to have a great capability to reduce a filler-filler interaction and improve the reinforcing ability of clay compared to APTES (Siriwong et al., 2013). The influence of filler though is important, yet in order to achieve desired properties in some cases, the blends of two or more elastomer are preferred. EPDM have low saturated rubbers with a small concentration of nonconjugated diene. They impart good resistance especially towards oxidation, ozone and heat. This thus made them being preferred the most in outdoor applications but their poor resistance to fatigue limits their use in vibration application such as automotive engine mounts. Therefore, in order for EPDM/Bt composites to have good properties in both fatigue life and also thermal stability, NR was blended with EPDM (which is widely known having an excellent resistance to fatigue). Earlier study from Mathialagan and Ismail, (2011) have been focusing on the improvement of properties of EPDM/Bt composites in term of its curing characteristics, tensile and thermal properties where the improvement in terms of their tear strength, aging resistance and fatigue life have not been touched. This research would be a continuous work based on similar EPDM/Bt composites used but with different approach of testing to further investigate the ability of incorporation of Bt as a reinforcing filler in EPDM composites. In this present work, Bt and Si69 loading, as well as the loading of Bt/$CaCO_3$ ratio and EPDM/NR blend ratio on the curing characteristics, tear strength, aging properties and fatigue life of EPDM composites are studied to further investigate the potential use of Bt as a reinforcing filler in EPDM composites.

1.3 Objectives of Study

1. To investigate the effect of Bt loading on the curing characteristics, tear strength, aging resistance, and fatigue life of EPDM/Bt composites.
2. To investigate the effect of partial replacement of Bt by $CaCO_3$ on the processing characteristics and properties of EPDM composites.
3. To determine the effect of silane coupling agent, Si69 on the processing characteristics and the properties of EPDM/Bt composites.
4. To determine the effect of EPDM/NR blend ratio on the processing characteristics and the properties of EPDM/Bt composites.

1.4 Scope of Study

The focus of the work was to investigate the curing characteristics, mechanical and aging properties based on bentonite filled EPDM composites. There are two mechanical properties investigated in this work which are tear strength and fatigue life. SEM morphology was studied to prove any development in the properties. The work was divided into several parts and as follows:

1. Effect of Bt loading on the properties of EPDM/Bt composites.

   This part will focus on the preparation and the work to prove the possibility of Bt to be used as a filler in EPDM composites. The loading of Bt was varied in order to see any development in properties with increasing of Bt in rubber composites. SEM morphology was

used to prove the possible reinforcement by Bt. Optimum Bt loading that can obtain the highest properties of the composites was also determined along the study.

2. Partial replacement of Bt by $CaCO_3$ as filler in EPDM/Bt composites.

   The use of $CaCO_3$as a partial replacement to Bt was investigated. Loading ratio of Bt to $CaCO_3$ was varied to compare the possible reinforcement by these two fillers in EPDM/$CaCO_3$/Bt composites.

3. In situ addition of si-69 on the properties of EPDM / Bt composites

   Silane coupling agent was utilized to improve the properties of the rubber composites. Si-69 was used and added via in-situ method to improve the adhesion of Bt to EPDM matrix. Optimum loading of Si-69 that can achieve highest reinforcement was determined from the study. SEM was used to prove any possible increase in the properties of EPDM/Bt composites.

4. The effects of EPDM/NR blend ratio on the properties of EPDM/NR/Bt composites.

   Any possible reinforcement with the use of different blend ratio of NR and EPDM rubber on the curing characteristics and the properties EPDM/NR/Bt composites was determined in the study.

1.5 Thesis Organization

There are five chapters in this thesis. The chapters are as follows:

- **Chapter one** focuses on the introduction to the thesis. The introduction consists of the overview of the thesis in general, follows by problem statements, the main objectives, the importance of this research, as well as the scope of study and the thesis organization.
- **Chapter two** covers the literature reviews related to the research work particularly EPDM/Bt composites. It also includes the general introduction about EPDM and NR, and fillers used which are bentonite, and calcium carbonate.
- **Chapter three** gives the information about the materials used in this research. It also includes the compound formulations and experimental procedures to prepare the composites as well as the testing used to evaluate the properties obtained for each of the composites.
- **Chapter four** contains discussions on the effect of bentonite, Bt/$CaCO_3$ loading ratio, Si69 loading and EPDM/NR blend loading ratio on the processing characteristic and mechanical properties of the composites.
- **Chapter five** concludes the findings of this research work and some recommendations for future work.

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

A rubber composite that is able to act as multi-functional materials is one of the reasons that there were a vast journal articles that can be found related to the study of rubber composites. This is because they are capable in improving not only one but some of the properties of the individual materials. This is a very desirable especially to the researchers in order for the materials to meet the requirement in certain applications especially the one that need the materials to be lightweight and durable such in aircraft. The use of rubber composites also is very useful in producing low-cost materials and this is why composites were actually being preferred more to be used as a replacement or combination to other materials in producing products. The use of clay able to enhance the properties of the nanocomposites and even better than the use of carbon black which was more established and popular among other type of filler due to its reinforcing capability. Not only that, the use of clay is very desirable as it can be used to alter the final colour of the product which is however limited with the use of carbon black. In this chapter, the overviews around clay based EPDM composites will be presented.